HPLC-FTIR ANALYSIS OF POLAR COAL-DERIVED MATERIAL

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INTRODUCTION

The detailed analysis of coal-derived products (CDP) is hampered by several factors. Their composition is not only extremely complex but also extremely heterogeneous as to component classes. Unlike petroleum products, most of the CDP is of relatively high molecular weight and exhibits a relatively large heteroatom (N,O,S) content. In addition, a major portion of the CDP is non-distillable which does not permit the use of many of the procedures previously developed for the analysis of crude oils. In this regard, different methods of analysis are required. For the nonvolatile CDP fractions, these analytical techniques are still in the exploratory stage. A combined condensed phase separation-spectrometric means of analysis seems especially suited for these materials. On-line analysis also appears highly attractive in view of the heterogeneous nature of the precursor feed coals and the desirablility of rapid, discriminatory analytical procedures by the coal conversion industry. Depending on the functionalities of interest, a variety of combination techniques (separation-spectrometric) can be envisioned for nonvolatile CDP's.

Various spectroscopic techniques applied to isolated fractions have provided detailed structural information but each suffers from not being able to distinguish individual components. The coupling of HPLC separations directly with highly information-specific spectrometric detectors "on-line" may provide the potential for the identification of many of the components of these complex mixtures. Infrared spectrometry yields characteristic and often specific absorbances for many organic functionalities and particularly for many of the heteroatom containing compounds which need to be analyzed. IR also seems a very logical choice as a detector for the HPLC separation of CDP's since it is easily adapted to a flowing stream. We wish to describe the application of a HPLC-FTIR system to a coal-derived residuum.

RESULTS AND DISCUSSION

The coal-derived samples employed in this study were received from the Kerr McGee Corporation. Liquefaction conditions were as follows:

Wyodak #3 feed coal
100% THQ; S:C, 2:1
1100 psi H_2, 30 minutes, 785°F

After the reaction was terminated, gases were vented from the reactor and the reaction vessel was emptied of its contents. Some residuum and process solvent remained in the vessel. This material was removed by washing the vessel with tetrahydrofuran (THF). Material which was solubilized in this way was designated THF solubles. A preliminary preparative separation on the THF solubles was performed in order to remove the relatively large amount of 1,2,3,4-tetrahydroquinoline (THQ) known to be present in the THF-solubles sample. Fraction 1, eluted with hexane, was indeed found to contain almost exclusively THQ. Fraction 2 whose analysis is described below contained only a small amount of THQ.

A microbore scale chromatographic separation of fraction 2 with UV and FTIR detection is shown in Figure 1. Upon examination of the UV trace, it is seen that most peaks elute in the same region as previously found for simple basic nitrogen model compounds. The numbers over the peaks in Figure 1B correspond to individual

spectra obtained throughout the HPLC-FTIR run. There is a large amount of saturation reflected in each file spectrum as evidenced by the relatively intense CH stretching modes between 2800 and 3000 cm^{-1}. This is perhaps an indication of alkyl side chains on an aromatic ring. Two major components in this fraction are THQ (file 203) and quinoline (file 225). File 201 indicates the presence of N-methylaniline as shown by its comparison with the spectrum of the model compound. Obviously, another component(s) is also represented in file 201 since the two spectra do not perfectly agree. Some of the other files have not been identified although these contain bands consistent with nitrogen heterocyclic compounds. A match with model compound spectra has not been made. The spectrum corresponding to file 235 is interesting. The component represented in this file elutes after quinoline, but it is not resolved from quinoline. This spectrum contains a weak NH stretch, and rather intense C=C and C=N bands at 1598 cm^{-1} and 1500 cm^{-1} in addition to two bands at 1324 cm^{-1} and 1296 cm^{-1}. The material giving rise to this spectrum is suspected to be due to a THQ dimer This component will be examined in further detail when the fraction's mass spectrum is discussed.

A survey of all files indicated the presence of several different carbonyl species. Figure 2 shows the carbonyl stretching region (1800-1600 cm^{-1}) for selected spectra taken throughout the entire run. The band at 1600 cm^{-1} which is present in every file is due to an aromatic C=C ring stretch. Early in the run (file 190), before elution of THQ, bands at 1677 and 1690 cm^{-1} are observed. These bands are seen in all files up to 201. After THQ elutes (file 203) an unique band at 1660 cm^{-1} is seen in file 217 prior to elution of quinoline (file 225). Finally, compounds elute between files 244-250 with a characteristic FTIR absorbance at 1774 cm^{-1}.

A tertiary amide exhibits a band near 1650 cm^{-1}. This could correspond to the band in file 217 but not file 190. A type of ketone is also possible. Our preferred assignment is that hydroxypyridine or a similar compound could be responsible for the IR absorbance in this region. Many of these types of compounds exist exclusively in the keto form. Enamines such as tetrahydropyridine are known to be susceptible to reaction with oxygen to yield similar type compounds. A similar kind of reaction could well be occurring with THQ during liquefaction. Single injections of 2-hydroxypyridine and 4-hydroxypyridine support this assignment in that these compounds elute with retention times similar to those of compounds found in files 190-217. Figure 3 shows the IR spectrum of 2-hydroxypyridine and 4-hydroxypyridine for comparison will file spectra 190 and 217.

The 1774 cm^{-1} band in files 244-250 is higher in frequency than is seen in many types of carbonyl compounds and is therefore more easily assigned. A five-membered γ-lactone has a band at 1770 cm^{-1}. The presence of such a species is likely since THF was used to isolate the original sample. It is known that in the presence of coal-derived material THF adducts readily to the coal material and can be converted to γ-butyrolactone under rather mild conditions.

To confirm assignments made on the basis of HPLC-FTIR as well as to gain additional information, THF solubles fraction 2 was subjected to field ionization mass spectrometry (FIMS). The sample was 100% volatile in the spectrometer in the temperature range employed (48-451°C). Spectra were collected over eight temperature ranges and these were then summed into one over-all spectrum. This composite spectrum is shown in Figure 4. The number average molecular weight is 328 for this fraction and the weight average molecular weight is 396. An overall ratio of odd to even mass peaks equal to 0.84 was calculated for this sample. It appears from this O/E ratio that almost half the material in fraction 2 contains an odd number of nitrogen atoms.

Examining the individual temperature ranges affords more information than an examination of the summed spectrum alone. Each temperature gives rise to a spectrum that is simpler than the composite spectrum since all the compounds are not present

in each range. The first temperature range examined (48-83°C) has an O/E ratio of 4.36. Obviously, compounds having an odd number of nitrogen atoms dominate. The most intense peaks are THQ (m/e = 133) and quinoline (m/e = 129). These compound assignments can be confidently made (as opposed to the isomers 1,2,3,4-tetrahydro-isoquinoline and isoquinoline) because of the information obtained from HPLC-FTIR. Also, from the FTIR analysis, N-methylaniline can be said to be at least in part responsibile for the peak at 107. The other possible isomers of m/e = 107 were not observed by FTIR.

FIMS suggests the presence of compounds not indicated by FTIR. These include indole or propylpiperidine (m/e=117) and their homologues (m/e = 131), ethylaniline or a C_1 homologue of mass 107 (m/e = 121) and indanol (m/e = 134). Some compounds indicated by FIMS may also have been suggested by the FTIR analysis but a lack of model compounds and/or spectral library prevented exact assignment. For example, these might include homologues of THQ and quinoline (m/e = 143, 147, 157, 161). A hydroxyquinoline is suggested at mass 145 which supports an earlier assignment made via HPLC-FTIR.

In the second temperature range (87-110°C), in addition to compounds seen in the first temperature range, compounds of higher molecular weight are detected. The O/E ratio changes dramatically due to the nature of the compounds being volatilized during this temperature range. The O/E ratio is now 0.96. In the third temperature range (110-122°C) the O/E ratio decreases even further to 0.49. The mass peaks increasing most in intensity during the second and third temperature ranges are m/e = 260-266. With the exception of THQ, these peaks are the most intense ones in the FIMS summed spectrum. The suggested compounds for m/e = 260-266 are dimers of THQ and related "phenylquinoline-type" compounds.

The presence of such compounds in coal liquefaction products has been previously speculated. It has been noted that nitrogen-containing liquefaction solvents, while enhancing the liquefaction process by increasing the amount of soluble product, also produced non-distillable products and resulted in severe solvent loss. The suggestion was made that the liquefaction solvent was being incorporated into the coal structure or otherwise reacting to produce higher molecular weight materials. Unidentified IR spectra obtained by HPLC-FTIR can be associated with compounds of m/e 260-266 found in the FIMS spectra. Model compounds are unfortunately unavailable for exact assignment by either method.

In the higher temperature ranges, the O/E ratio approaches 1.00. This suggests that each high molecular weight specie has been "tagged" with THQ. As seen from the summed spectrum in Figure 4, these high mass peaks (> m/e = 320) are not very intense. Such high mass peaks could be due to trimers of THQ and related compounds.

ACKNOWLEDGMENTS

Figure 1

COLUMN: Microbore NH₂
MOBILE PHASE: 70:30
CDCl₃:CCl₄ + 0.02% TEA
FLOW RATE: 35 µL/MIN

A

DETECTOR: UV (254 NM)

B

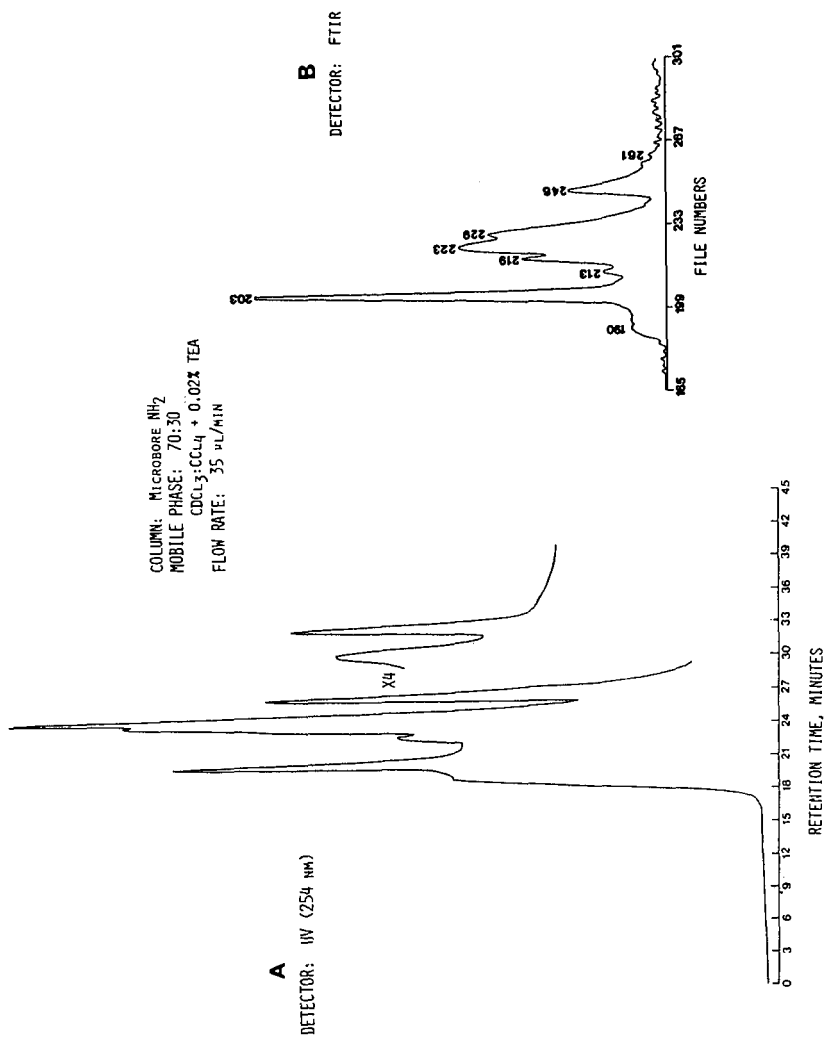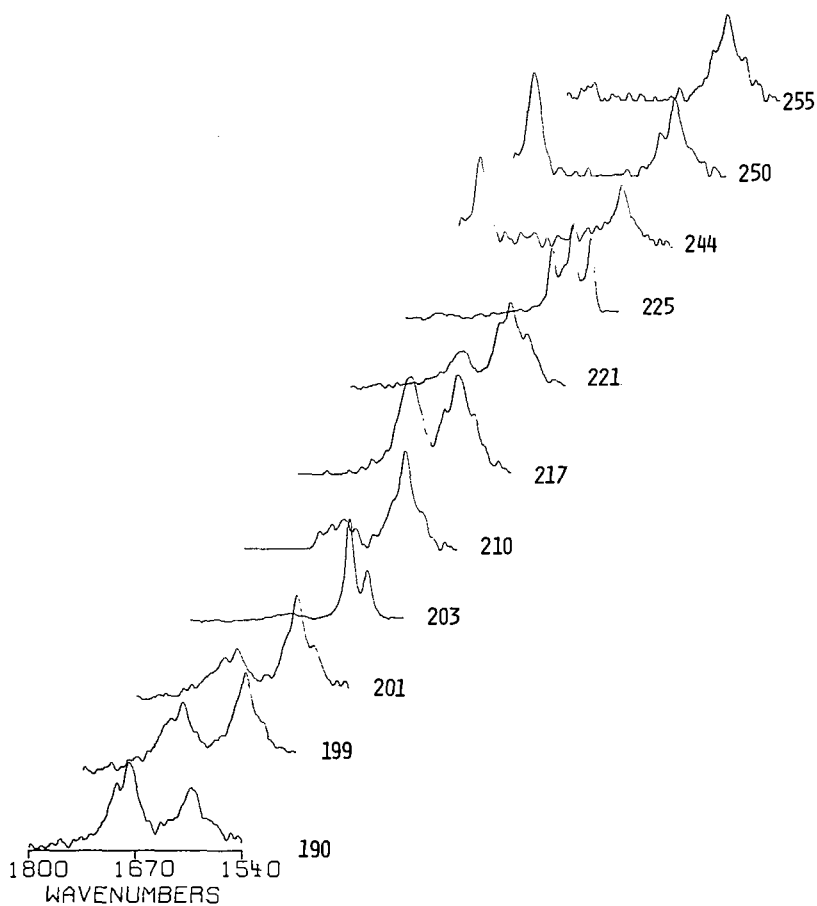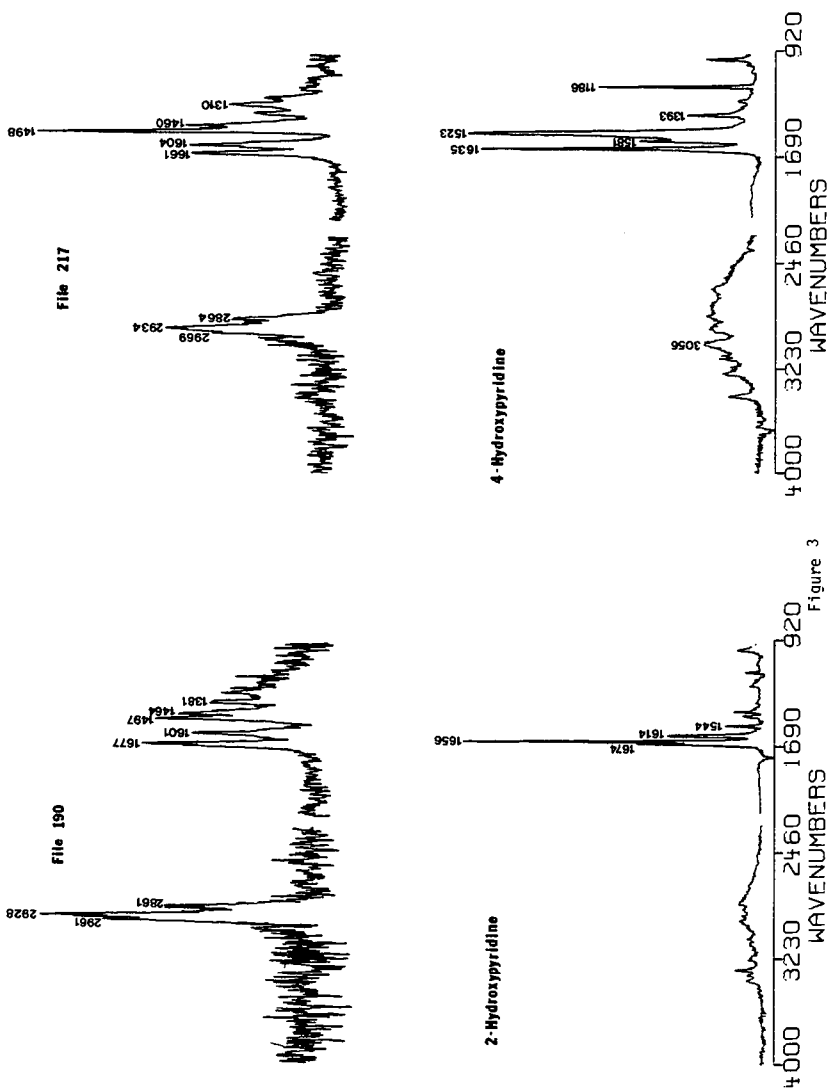DETECTOR: FTIR

FILE NUMBERS

RETENTION TIME, MINUTES

Figure 2. Carbonyl stretching region for selected spectra obtained during the separation of THF Solubles fraction 2.

Figure 3

R31104.SUM   T = 48 TO 451 DEG C'   N AV MW=328   WT AV MW=396
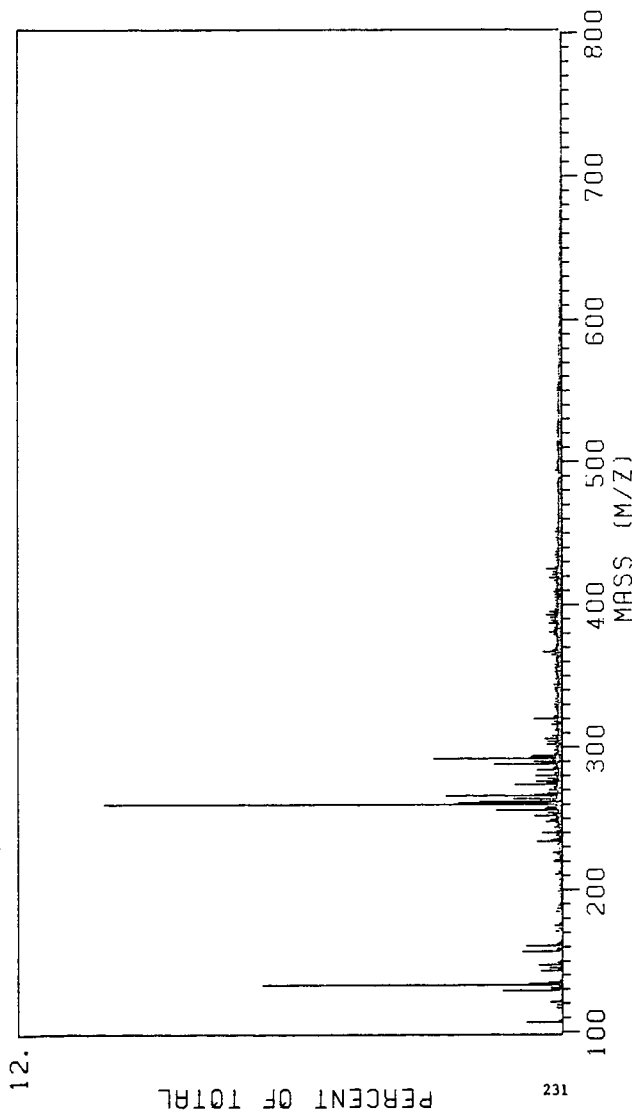VPI-AMATEIS, THF SOLUBLE, FRACTION #2   1 - 8

12.

PERCENT OF TOTAL

MASS (M/Z)

Figure 4

SRI FIMS V2.3

20-DEC-83   15:27:32

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